

VERIFICATION OF TRANSLATION

I, Shuji Sawada, of 2-34-1710, Heso 2-chome, Ritto-shi, Shiga 520-3031 Japan hereby declare that I am competent in both the Japanese and English languages and that the attached English language translation, which is identified as Docket No. 61A27490-A, is an accurate translation of Japanese Patent Application No. 2002-308048.

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[Title of the Invention] NANOFIBER

[Claims]

[Claim 1] An aggregate of nanofibers having a morphology like filament-yarn and/or a morphology like spun yarn, wherein single fiber fineness by number average is in a range from 1×10^{-7} to 1×10^{-4} dtex and 60%, in fineness ratio, or more of single fibers are in a range from 1×10^{-7} to 1×10^{-4} dtex in single fiber fineness.

[Claim 2] An aggregate of nanofibers comprising a polymer made through polycondensation, wherein single fiber fineness by number average is in a range from 1×10^{-7} to 1×10^{-4} dtex and 60%, in fineness ratio, or more of single fibers are in a range from 1×10^{-7} to 1×10^{-4} dtex in single fiber fineness.

[Claim 3] The aggregate of nanofibers according to claim 1 or 2, wherein 50%, in fineness ratio, or more of nanofibers are in a section having a width of 30 nm in diameter of the single fibers.

[Claim 4] The aggregate of nanofibers according to any one of claims 1 to 3, wherein melting point is 165°C or higher.

[Claim 5] The aggregate of nanofibers according to any one of claims 1 to 4 that includes polyester, polyamide or polyolefin in at least a part thereof.

[Claim 6] The aggregate of nanofibers according to any one of claims 1 to 5, that has a strength of 1 cN/dtex or higher.

[Claim 7] The aggregate of nanofibers according to any one

of claims 1 to 6, that has a ratio of moisture adsorption of 4% or higher.

[Claim 8] The aggregate of nanofibers according to any one of claims 1 to 7, that has a rate of elongation at absorbing water of 5% or higher in the longitudinal direction of the yarn.

[Claim 9] A fibrous article that has the nanofibers according to any one of claims 1 to 8 included in at least a part thereof.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention]

The present invention relates to an aggregate of nanofibers having little spread of single fiber fineness values that has been unprecedented in the prior art.

[0002]

[Prior Art]

Polymers manufactured through polycondensation such as polyester typified by polyethylene terephthalate (PET) and polybutylene terephthalate (BT), and polyamide typified by nylon 6 (N6) and nylon 66 (N66) have been preferably used in such applications as clothes and industrial materials, because of the favorable mechanical properties and heat resistance of these fibers. Polymers manufactured through addition polymerization typified by polyethylene (PE) and

polypropylene (PP), in contrast, have been preferably used mainly in industrial applications, because of the favorable mechanical properties, resistance to chemicals and lightness of these fibers.

[0003]

The polyester fiber and the polyimide fiber, in particular, have been used in the applications for clothes and therefore have been subjected to vigorous researches for not only to modify the polymer but also to improve the properties by controlling the cross sectional shape of the fiber or using an extremely fine fiber. One of such attempts resulted in ultrafine polyester fibers made by using an islands-in-sea multi-component fiber, that was used in an epoch making new product of synthetic leather having the touch of suede. These ultrafine fibers have been applied to the manufacture of ordinary clothes, and are used in the development of clothes that have excellent hands like peach skin which can never be obtained with ordinary fibers. The ultrafine fibers, those have found applications not only for clothes but also for livingwares such as wiping cloth and industrial materials, have secured a position of its own in the area of synthetic fibers today. Recently, in particular, applications of the ultrafine fibers have been expanded to texturing cloth for the surface of a computer hard disk as described in Japanese Unexamined Patent Publication No. 2001-

1252 and Japanese Unexamined Patent Publication No. 2002-224945, and medical supplies such as cell adsorbing material as described in Japanese Unexamined Patent Publication No. 2002-102332 and Japanese Unexamined Patent Publication No. 2002-172163.

[0004]

Accordingly, there has been demand for further finer fibers in order to make a synthetic leather of higher quality and clothes of excellent feeling. In the meantime, efforts are being made to increase the storage capacity of hard disks as the basis for the advance of IT industry. In order to increase the storage capacity of a hard disk with increased recording density, it is necessary to make the surface of the hard disk smoother from the mean surface roughness of 1 nm or more at the present to 0.5 nm or less. For this purpose, nanofibers having further decreased thickness have been required to make a texturing cloth for texturing the hard disk surface.

[0005]

However, the prior art islands-in-sea multi-component spinning technology has a limitation of 0.04 dtex (equivalent diameter 2 μm) for improving the single fiber fineness, which cannot fully meet the needs for the nanofibers. While there are methods for making ultrafine fibers from polymer blend fibers (Patent Documents 1, 2), a single fiber fineness that

can be achieved by these technologies is 0.001 dtex (equivalent diameter 0.4 μm) at the best, which also cannot fully meet the needs for the nanofibers. Moreover, while the single fiber fineness of the ultrafine fibers made by these methods is determined by the state of dispersion of the island polymer in the polymer blend fibers, the polymer blend system described in the Patent Document has a large spread of single fiber fineness values of the resultant ultrafine fibers due to insufficient dispersion of the island polymer in the polymer blend fibers. As a result, property of the product is determined by thick single fibers, failing to make full advantage of the properties of the ultrafine fibers and stabilize the product quality. In addition, when used as a texturing cloth for texturing the hard disk surface, the large spread of fineness values makes it impossible to support abrasive particles evenly on the texturing cloth, thus resulting in such a trouble that the use of the texturing cloth results in the hard disk surface becoming less smooth, contrary to the intention.

[0006]

Meanwhile a technology called the electrospinning has been in spotlight as a promising technology that can manufacture ultrafine fibers. The electrospinning is a process in which a polymer is dissolved in an electrolysis solution and is extruded through a spinneret while applying a

high voltage to the polymer solution, so as to split the polymer solution by the force of electrostatic repulsion into ultrafine fibers. This technology may produce, depending on the circumstance, yarns having a single fiber fineness on the order of 10^{-5} dtex (equivalent single fiber diameter several tens of nanometers), that is one hundredth or less in fineness and one tenth or less in diameter of the yarn produced by the conventional polymer blending technology. However, the polymers which can be processed by this technology are limited to those that can be dissolved in electrolysis solution, and it has been difficult to apply the electrospinning technology to the general-purpose polymer of polyester and thermoplastic polymers such as polyamide and polyolefin. While it is studied to apply the electrospinning technology to molten thermoplastic polymer, there are such problems that the polymer hardly conducts electricity and cannot be charged with sufficient electrostatic charges, and the molten polymer has high viscosity and is difficult to split. As a result, what can be made with this technology is yarns having a single fiber fineness on the order of 10^{-2} dtex, coarser even when compared to the conventional islands-in-sea multi-component spinning technology. Furthermore, application of the electrospinning known in the prior art results in strings that constitute the ultrafine fibers are often connected by beads (about 0.5 μm in diameter) that is

formed from a stagnant polymer drop, thus resulting in a large spread of single fiber fineness values in an aggregate of ultrafine fibers (non-Patent Document 1). Since the property of the product is determined by thick single fibers, it is not possible to make full advantage of the ultrafine fibers and stabilize the product quality. In addition, when used as a texturing cloth for texturing the hard disk surface, as described previously, the large spread of fineness makes it impossible to support abrasive particles evenly on the texturing cloth, thus resulting in such a trouble that use of the texturing cloth results in larger surface roughness of the hard disk surface, contrary to the intention. Fibers and fibrous articles that can be manufactured by electrospinning is limited to unwoven fabrics, thus placing great restrictions on the application of the technology.

[0007]

There is an atypical method for manufacturing nanofibers, according to which a polymerization catalyst is supported on a meso-porous silica so as to polymerize PE thereon, thereby to produce PE nanofiber measuring 30 to 50 nm (equivalent to 5×10^{-6} dtex to 2×10^{-5} dtex) in diameter (non-Patent Document 2). However, what can be obtained with this method is mere wad-like aggregate of nanofibers, which makes it impossible to draw a fiber therefrom. Also the polymer that can be processed with this method is limited to

PE manufactured through addition polymerization. Polymers manufactured through polycondensation such as polyester and polyamide require dehydration in the process of polymerization, and there is a fundamental difficulty for applying the method to these fibers. Thus there has been a significant hurdle for practical application of the nanofibers obtained by this method.

[0008]

With the background described above, there have been demands for nanofibers having little spread of single fiber fineness values, which impose no restriction on the form of fiber or the fibrous product and on the kind of polymer, and can be put in diverse applications.

[0009]

[Patent Document 1]

Japanese Unexamined Patent Publication No. 3-113082 (pp.1-5)

[0010]

[Patent Document 2]

Japanese Unexamined Patent Publication No. 6-272114 (pp.1-7)

[0011]

[Non-Patent Document 1]

Polymer, vol.40, 4585 (1999)

[0012]

[Non-Patent Document 2]

Science, vol.285, 2113 (1999)

[0013]

[Problems to be Solved by the Invention]

The present invention aims to provide nanofibers having little spread of single fiber fineness values, which impose no restriction on the form of fiber or the fibrous articles and on the kind of polymer, and can be put in diverse applications.

[0014]

[Means for Solving the Problems]

The object described above can be achieved by an aggregate of nanofibers, wherein single fiber fineness by number average is in a range from 1×10^{-7} to 1×10^{-4} dtex and single fibers of 60%, in fineness ratio, or more of single fibers are in a range from 1×10^{-7} to 1×10^{-4} dtex in single fiber fineness, having a morphology like filament-yarn and/or a morphology like spun yarn, or an aggregate of nanofibers made through polycondensation, wherein the single fiber fineness by number average is in a range from 1×10^{-7} to 1×10^{-4} dtex and single fibers of 60%, in fineness ratio, or more of single fibers are in a range from 1×10^{-7} to 1×10^{-4} dtex in single fiber fineness.

[0015]

[Embodiments of the Invention]

While the polymer in the present invention refers to thermoplastic polymers such as polyester, polyamide and

polyolefin, thermosetting polymers such as phenol resin and bio-polymers such as DNA, thermoplastic polymers are preferably used for the reason of moldability. Among these, polymers manufactured through polycondensation typified by polyester and polyamide are often characterized by high melting point and are more preferably used. It is preferable that the polymer has a melting point of 165°C or higher, since it results in high heat resistance of the resultant nanofibers. For example, melting point of polylactic acid (hereinafter abbreviated as PLA) is 170°C, that of PET is 255°C, and that of N6 is 220°C. The polymer may include particles, flame retarding agent, antistatic agent or the like added thereto. The polymer may also be copolymerized with other component to such an extent that the property of the polymer is not compromised.

[0016]

The nanofiber referred to in the present invention is a fiber having single fiber diameter in a range from 1 to 250 nm. An aggregate of such fibers is called the aggregate of nanofibers. According to the present invention, a mean value and spread of single fiber fineness values in the aggregate of nanofibers are important factors. A single fiber diameter is measured for 300 or more single fibers that are randomly sampled in the same cross section, through observation of the cross section of the aggregate of nanofibers with a

transmission electron microscope (TEM). This measurement is made in at least five places, so as to measure the diameters of 1500 or more single fibers in all, thereby to determine the mean value and spread of single fiber fineness values in the aggregate of nanofibers. Positions to make these measurements are preferably separated by a distance of 10 m or more from each other, in order to ensure the uniformity of the fibrous article to be made from the aggregate of nanofibers.

[0017]

Mean value of the single fiber fineness is determined as follows. Fineness is calculated from the measured diameter of the single fiber, and these values are averaged. This mean value is referred to as "the single fiber fineness by number average" in the present invention. According to the present invention, it is important that the single fiber fineness by number average is in a range from 1×10^{-7} to 1×10^{-4} dtex (equivalent to single fiber diameter from 1 to 100 nm). This is as thin as 1/100 to 1/100000 that of the ultrafine fiber made from the conventional islands-in-sea multi-component fiber, and enables it to make fabric for clothing that has touch feeling completely different from that of the ultrafine fibers of the prior art. When used as a texturing cloth for hard disk, it can make the hard disk surface far smoother than in the prior art. The single fiber

fineness by number average is preferably in a range from 1×10^{-5} to 6×10^{-5} dtex (equivalent to single fiber diameter from 40 to 80 nm).

[0018]

Spread of single fiber fineness values of the nanofibers is evaluated as follows. Single fiber fineness dt_1 of each single fiber is totaled to obtain the total fineness ($dt_1 + dt_2 + \dots + dt_n$). Product of a value of single fiber fineness and the number of nanofibers that have this same value of fineness divided by the total fineness is called the fineness ratio of this value of single fiber fineness. The fineness ratio corresponds to the weight proportion (volume proportion) of each single fiber fineness component to the population (aggregate of nanofibers). The larger the fineness ratio, the greater contribution the single fiber fineness component has to the property of the aggregate of nanofibers. According to the present invention, it is important that single fibers of 60%, in fineness ratio, or more of single fibers are in a range from 1×10^{-7} to 1×10^{-4} dtex in single fiber fineness (equivalent to single fiber diameter from 1 to 100 nm). This means that nanofibers larger than 1×10^{-4} dtex (equivalent to single fiber diameter of 100 nm) are substantially nonexistent. This makes it possible to fully demonstrate the functions of the nanofiber, and allows it to manufacture articles having high

stability of quality. When used to make the texturing cloth for hard disk surface, the small spread of fineness values of the aggregate of nanofibers enables it to bear abrasive particles uniformly on the texturing cloth, thus resulting in a dramatic improvement in the smoothness of the hard disk surface. Single fibers of 60%, in fineness ratio, or more are preferably in a range from 1×10^{-7} to 6×10^{-5} dtex (equivalent to single fiber diameter from 1 to 80 nm). More preferably, single fibers of 75%, in fineness ratio, or more are in a range from 1×10^{-7} to 6×10^{-5} dtex (equivalent to single fiber diameter from 1 to 80 nm)

[0019]

Another measure of the spread of fineness values is the fineness ratio of the single fibers that fall within a section having a width of 30 nm in diameter of the single fiber. The fineness ratio represents the concentration of fineness values around the median fineness. Higher the fineness ratio in the section, the smaller the spread becomes. According to the present invention, the fineness ratio of the single fibers that fall in the section having a width of 30 nm is preferably 50% or more, more preferably 70% or more.

[0020]

According to the present invention, it is preferable that the aggregate of nanofibers has a morphology like filament-yarn and/or a morphology like spun yarn. The phrase

"a morphology like filament-yarn and/or a morphology like spun yarn" means such a state of an aggregate of a plurality of nanofibers that are oriented one-dimensionally and continue over a definite length. A nonwoven fabric made by electrospinning has an entirely different form of two-dimensional aggregate where the nanofibers are disposed without any orientation. The present invention has novelty in that the aggregate of nanofibers has one-dimensional orientation. The length of the aggregate of nanofibers of the present invention, having a morphology like filament-yarn and/or a morphology like spun yarn, is preferably several meters or longer, as in the case of the conventional filament-yarn and/or spun yarn. This constitution enables it to make various fibrous materials such as short fibers, nonwoven fabric and heat compression-formed article, as well as woven fabric and knitted fabric.

[0021]

The aggregate of nanofibers of the present invention, because of the single fiber diameter as small as 1/10 to 1/100 that of the ultrafine fiber of the prior art, has dramatically increased the specific surface area. As a result, it demonstrates properties characteristic of the nanofiber which the conventional ultrafine fibers did not show.

[0022]

For example, the aggregate of nanofibers shows greatly improved adsorbing capability. In a comparison of water vapor adsorbing capability, namely moisture adsorbing capability between the polyamide aggregate of nanofibers of the present invention and the conventional ultrafine polyamide yarn, the polyamide aggregate of nanofibers of the present invention showed the ratio of moisture adsorption as high as 6% while the conventional ultrafine polyamide yarn has the ratio of moisture adsorption of about 2%. Moisture adsorption capability is a very important property for clothing articles, in order to provide comfort of wear. According to the present invention, the ratio of moisture adsorption is preferably 4% or higher.

[0023]

Moreover, since the aggregate of nanofibers of the present invention has numerous voids that measure several nanometers to several hundreds of nanometers between the single nanofibers, the aggregate of nanofibers may demonstrate a unique property such as that of an ultra-porous material.

[0024]

For example, while the conventional polyamide ultrafine fibers show a rate of elongation at absorbing water of about 3% in the longitudinal direction of yarn, the aggregate of polyamide nanofibers of the present invention can show a rate

of elongation at absorbing water as high as 7%. Moreover, the aggregate of nanofibers returns to the original length when dried after the elongation at absorbing water, the change in size is reversible. The reversible elongation in the longitudinal direction of yarn upon absorbing water/drying is an important property in view of soil releasing capability of cloth. According to the present invention, the ratio of elongation is preferably 5% or higher. The soil releasing capability refers to the capability of the cloth to get rid of stain when laundered. Since the aggregate of nanofibers elongates in the longitudinal direction of yarn upon absorbing water with the voids between the fibers (space between the fibers) in the woven fabric or the knitted fabric being expanded, stain sticking to the fibers can be easily removed.

[0025]

The aggregate of nanofibers of the present invention, when used in clothing applications, can produce fibrous articles having excellent hands such as sleekness of silk or dry feeling of rayon. Furthermore, fibrous articles that have ultra-soft feeling like peach skin, or soft and moist touch like human skin which have never been realized can be provided by separating the nanofibers from the aggregate of nanofibers by buffing or other process.

[0026]

While there is no restriction on the method for manufacturing the aggregate of nanofibers of the present invention, a method described below, for example, can be employed.

[0027]

Two or more kinds of polymer having different levels of solubility to a solvent are alloyed, so as to form a molten polymer alloy that is spun and is cooled to solidify, thereby forming fibers. The fibers are subjected to drawing and heat treatment as required, thereby to obtain polymer alloy fibers. Then the aggregate of nanofibers of the present invention can be made by removing the high solubility polymer from the polymer alloy fibers by means of a solvent.

[0028]

While the polymer alloy fiber that is the precursor for the aggregate of nanofibers has islands-in-sea structure consisting of a high solubility polymer as the sea component (matrix) and a low solubility polymer as the island component (domain), it is important to control the size of the island component. Size of the island component is determined by observing a cross section of the polymer alloy fiber under a transmission electron microscope (TEM) and giving the size in terms of equivalent diameter. Since diameter of the nanofiber is roughly determined by the size of the island component in the precursor, distribution of island sizes can

be designed in accordance to the distribution of diameters of the nanofibers of the present invention. Therefore, it is very important to mix and knead the polymers to be alloyed and, according to the present invention, it is preferable to carry out high level of mixing and kneading by means of an extrusion kneader or a static mixer. In the case of the simple chip blending (Patent Document 2), the materials are not sufficiently mixed and kneaded and therefore it is difficult to disperse the islands having sizes of several tens of nanometers as in the present invention.

[0029]

While proper mixing operation depends on the combination of polymers, it is preferable to use a twin-screw extrusion-kneader in case an extrusion-kneader is employed, or set the number of splits to 100×10^4 or more in case a static mixer is employed.

[0030]

The combination of polymers is an important factor to disperse the islands-part polymer at the order of several tens of nanometers.

[0031]

In order to form the island domains (section of nanofiber) having substantially circular cross sections, the island component and the sea component are preferably incompatible to each other. However, it is difficult to

disperse the nano-sized islands by simply using a combination of mutually incompatible polymers. Thus it is preferable to optimize the compatibility of the polymers to be combined, which can be indicated by the solubility parameter (SP value). The SP value is a parameter that represents the cohesion force of a material and is defined as $(\text{vaporizing energy/molar volume})^{1/2}$. Materials having proximate values of SP are likely to make a polymer alloy of good compatibility. SP values of various polymers have been known, and are given in, for example, "Plastic Data Book", coedited by Asahi Kasei AMIDAS Co., Ltd. and the editorial staff of the Plastics, p189. It is preferable that the difference in the SP value between two polymers is in a range from 1 to 9 $(\text{MJ/m}^3)^{1/2}$, which makes it easier to achieve both a circular cross section of the island domain and the dispersion of nano-sized islands through the use of incompatible polymers. A preferable example of combination is N6 and PET, of which SP values have a difference of about 6 $(\text{MJ/m}^3)^{1/2}$. An example of combination that is not preferable is N6 and PE of which SP values have a difference of about 11 $(\text{MJ/m}^3)^{1/2}$.

[0032]

In order to mix and knead with high efficiency, it is preferable that melting points of the island component polymer and the sea component polymer have a difference not larger than 20°C, in which case there occurs no significant difference in the melting of the polymers in the extrusion kneader. While it is necessary to control the mixing

temperature and the spinning temperature to low levels when a polymer that is susceptible to thermal decomposition and/or thermal degradation is used as one of the polymers, use of polymers having smaller difference in the melting point is advantageous also for solving this problem. In the case of amorphous polymer which does not have melting point, Vicat softening temperature is used instead of melting point.

[0033]

The melt viscosity is also an important factor. The island component tends to disperse on the order of nanometers due to a higher tendency of the island component to deform under a shear force, when the low solubility polymer that makes the island component has lower melt viscosity. However, an excessively low viscosity may turn the island component into sea component, making it difficult to achieve a high blending ratio of the entire fiber. Therefore, it is preferable that the melt viscosity of the polymer that makes the island component is 1/10 times or more of the melt viscosity of the polymer that makes the sea component.

[0034]

Since the island component and the sea component are incompatible to each other in the polymer alloy, the island components are more thermodynamically stable when cohered. However, in order to forcibly disperse the polymer as nano-sized islands, the polymer alloy has more polymer interfaces that are more unstable than a conventional polymer blend having larger dispersion sizes. As a result, when this

polymer alloy is simply spun, the existence of a number of unstable polymer interfaces leads to such problems as "Barus phenomenon" in which the polymer flow swells immediately after the polymer is discharged through the spinneret, and insufficient stringiness due to destabilization of the polymer alloy surface. This not only causes excessive thick-thin unevenness of the yarn but also makes it impossible to spin (negative effect of nano-sized polymer dispersion). In order to avoid such problems, it is preferable to control the shear stress between the spinneret orifice wall and the polymer being discharged through the spinneret. The shear stress between the spinneret orifice wall and the polymer is calculated by Hagen-Poiseuille's law that dictates that the shear stress (dyne/cm²) is given as $R \times P/2L$, where R is the radius of the spinneret orifice (cm), P is the pressure loss at the spinneret orifice (dyne/cm²) and L is the length of the spinneret orifice (cm). Pressure loss is calculated as $P = 8 L \eta Q / \pi R^4$, where η is the viscosity of the polymer (poise), Q is the discharge flow rate (cm³/sec) and π is the circular constant. In the melt spinning of the ordinary polyester, for example, while the shear stress between the spinneret orifice wall and the polymer is 1×10^6 dyne/cm² or higher, it is preferable to control the shear stress to 3×10^5 dyne/cm² or less in the case of melt spinning of polymer alloy as in the present invention. For this reason, there is a tendency to make the spinneret larger in orifice diameter and shorter in orifice length. However, when the diameter is increased

and/or the length is decreased excessively, weighability of the polymer at the spinneret orifice decreases while fineness unevenness and spinnability become worse. Therefore, it is preferable to use such a spinneret that has a polymer weighing section having an orifice provided above the spinneret orifice. Position of the polymer weighing section is preferably where the orifice diameter is reduced to be smaller than the discharge orifice.

[0035]

In order to ensure the stringiness and stability of spinning at sufficient levels during melt spinning, it is preferable to keep the surface temperature of the spinneret to 25°C or more higher than the melting point of the sea component.

[0036]

As described above, while it is important to properly design the spinneret for spinning the polymer alloy having uniformly dispersed constitution of nanometer sizes used in the present invention, it is also important to properly set the yarn cooling conditions. Since the polymer alloy is very unstable molten fluid as described above, it is preferably cooled and solidified immediately after being discharged from the spinneret. For this reason, distance between the bottom of the spinneret and the point where cooling begins is preferably in a range from 1 to 15 cm. The point where cooling begins is the position where positive cooling of the yarn begins, and it is assumed to be at the top end of the

cooling equipment in an actual melt spinning machine.

[0037]

While there is no limitation on the spinning rate, the spinning rate is preferably as high as possible, in order to achieve a high draft during the spinning process. The draft is preferably 100 or higher, in order to obtain nanofibers of smaller diameter.

[0038]

The polymer alloy fiber that has been spun is preferably subjected to drawing and heat treatment processes. Preheating temperature during drawing is preferably set not lower than the glass transition temperature (T_g) of the polymer that constitutes the island component for suppressing the occurrence of yarn unevenness.

[0039]

The manufacturing method of the present invention makes it possible to obtain polymer alloy fibers where the island component of several tens of nanometers is dispersed and yarn unevenness is very small, by optimizing the combination of the polymers, the spinning condition and the drawing condition as described above. By using the polymer alloy fiber, that has less unevenness in the longitudinal direction of yarn, as the precursor as described above, it is made possible to provide the aggregate of nanofibers that has small spread of single fiber fineness values in any of the sections in the longitudinal direction. It is preferable to control the Uster unevenness of the polymer alloy fiber,

which is the precursor, to 15% or less, more preferably to 5% or less.

[0040]

The aggregate of nanofibers is obtained by dissolving the high solubility polymer that is the sea component by means of a solvent from the polymer alloy fiber obtained as described above. In this process, it is preferable to use a water-soluble solvent in order to mitigate the load on the environment. Specifically, an aqueous alkaline solution or hot water is preferably used as the solvent. Accordingly, the high solubility polymer is preferably a polymer such as polyester that is hydrolyzed by alkali, or a polymer that is soluble to hot water such as polyalkylene glycol, polyvinyl alcohol or a derivative thereof.

[0041]

With the manufacturing method described above, the aggregate of nanofibers having a morphology like spun yarn, comprising nanofibers of several tens of micrometers, or may sometimes be on the order of centimeter, in length which are bonded or entangled with each other from point to point, is obtained.

[0042]

With the manufacturing method described above, particularly in case the static mixer is installed right above the spinneret, the aggregate of nanofibers having a morphology like filament yarn comprising nanofibers which may

be theoretically infinitely long.

[0043]

According to the method for manufacturing the aggregate of nanofibers of the present invention, unlike the nanofibers of the prior art, it is made possible for the first time to apply drawing and heat treatment to the nanofibers by applying drawing and heat treatment processes to the polymer alloy fiber that is the precursor. This has made it possible to control the tensile strength and the shrinkage ratio at will. It is preferable that the aggregate of nanofibers of the present invention has a strength of 1 cN/dtex or higher, or more preferably 2 cN/dtex or higher, which enables it to improve the mechanical properties of the fibrous articles. While the shrinkage ratio of nanofibers of the present invention can be adjusted in accordance to the application, heat-dry shrinkage ratio of nanofibers at 140°C is preferably not higher than 10% when used in clothing. Crimping treatment may also be applied to polymer alloy fiber that is the precursor.

[0044]

The aggregate of nanofibers of the present invention may be used in a variety of product forms such as long fiber, short fiber, unwoven fabric, or thermally molded articles, unlike the conventional ones. The aggregate of nanofibers of the present invention may be used, not only in clothing

applications such as shirts, blousons, pants or trousers, and coats, but also in wide applications including clothing materials such as cups and pads, interior applications such as curtains, carpets, mats as well as furniture, industrial materials such as filters and vehicle interior materials and medical supplies such as cell adsorbing material.

[0045]

Examples

Now the present invention will be described in detail by way of example. The physical properties in the examples were determined by the following methods.

[0046]

A. Melt Viscosity of Polymer:

The melt viscosity of a sample polymer was determined using Capillograph 1B available from Toyo Seiki Seisaku-Sho, Ltd. The residence time of the sample polymer from charging of the sample to the beginning of determination was set at 10 minutes.

[0047]

B. Melting Point:

The melting point was defined as the peak top temperature at which a sample polymer melted in a second run as determined using Perkin Elmer DSC-7 at a temperature scanning rate of 16°C per minute, with an amount of the sample of 10 mg.

[0048]

C. Shear stress at the spinneret orifice

The shear stress between the spinneret orifice wall and the polymer was calculated by Hagen-Poiseuille's law that dictates that the shear stress (dyne/cm²) is given as $R \times P/2L$, where R is the radius of the spinneret orifice (cm), P is the pressure loss at the discharge orifice of the spinneret (dyne/cm²) and L is the length of the spinneret orifice (cm). Pressure loss is calculated as $P = 8 L \eta Q / \pi R^4$, where η is the viscosity of the polymer (poise), Q is the discharge flow rate (cm³/sec) and π is the circular constant. While it is necessary to use the value of polymer viscosity under the conditions of temperature and shear rate of the spinneret orifice, there may be a case where it is difficult to determine the polymer viscosity through Capillograph measurement when a spinneret having a large discharge orifice is used since the shear rate becomes as low as 100 sec⁻¹ or less in this case. In such a case, the viscosity value was estimated by extrapolating the values measured at under conditions of higher shear rate or lower temperature.

[0049]

D. Uster Unevenness (U%) of Polymer Alloy Fiber:

The Uster unevenness was determined using USTER TESTER 4 available from Zellweger Uster in a normal mode at a yarn feed speed of 200 meters per minute.

[0050]

E. TEM Observation of Cross Section of Fiber:

Ultra-thin peaces of a sample fiber in a cross-sectional direction were prepared, and the cross sections of the fiber were observed using a transmission electron microscope (TEM). Nylon was subjected to metal staining using tungsten phosphate.

[0051]

TEM device: Model H-7100FA available from Hitachi, Ltd.

F. Single fiber Fineness and Single fiber diameter of Nanofibers by Number-average

The mean value of single fiber fineness was determined in the following manner. The diameters of single fibers and single fiber fineness were determined from TEM photographs of the cross section of the fiber using an image processing software (WINROOF), and the values were averaged. The mean values are defined as the diameters of single fibers and single fiber fineness by number average. Single fiber diameters of 300 or more nanofibers that were randomly sampled in the same cross section were measured to obtain the mean value. This measurement was made in at least five places separated by a distance of 10 m or more from each other, so as to measure the diameters of 1500 or more single fibers in all.

[0052]

G. Spread of Single fiber Fineness Values of Nanofibers

Spread of single fiber fineness values of the nanofibers is evaluated in the following manner. Single

fiber fineness dt_1 of each single fiber is totaled to obtain the total fineness $(dt_1+dt_2 + \dots + dt_n)$, using the data used in determining the single fiber fineness by number average. By counting the frequency (number) of nanofibers that have the same value of fineness, product of the value of single fiber fineness and the frequency divided by the total fineness is taken as the fineness ratio of single fiber fineness.

[0053]

H. Spread of Diameters of Nanofibers

Spread of diameters of the nanofibers is determined in the following manner. That is, the spread of diameters of the nanofibers is evaluated by the fineness ratio of the single fibers having a diameter which falls within a section having a width of 30 nm near the median of the single fiber diameter. This represents the concentration of the diameters around the median, and larger value thereof means less spread. This value of spread is also determined by using the data that were used to determine the single fiber fineness by number average.

[0054]

I. SEM Observation

Side surface of the fiber coated with platinum-palladium alloy by vapor deposition was observed under a scanning electron microscope.

[0055]

SEM device: Model S-4000 available from Hitachi, Ltd.

J. Mechanical Properties

Weight of 10 m segment of the aggregate of nanofibers was measured for five segments, and mean value thereof was used to determine the fineness (dtex) of the aggregate of nanofibers. Then at the room temperature (25°C), load-elongation curve was determined under the conditions specified in JIS L1013 with the initial sample length of 200 mm and drawing speed of 200 mm per minute. Then the load at rupture was divided by the initial fineness to give the strength. Elongation at break was divided by the initial sample length to give the elongation ratio, and accordingly the strength-elongation curve was determined.

[0056]

K. Ratio of Moisture Adsorption (ΔMR):

About 1 to 2 g of a sample is weighed in a weighing bottle, dried at 110°C for 2 hours, and the weight of the dried sample (W_0) is determined. Next, the sample substance is held at 20°C with relative humidity of 65% for 24 hours, and its weight is then measured (W_{65}), and the sample substance is then held at 30°C with relative humidity of 90% for 24 hours, and its weight is then measured (W_{90}). The ratio of moisture adsorption ΔMR is calculated according to the following equations.

[0057]

$$MR_{65} = [(W_{65} - W_0) / W_0] \times 100\% \quad (1)$$

$$MR90 = [(W90 - W0)/W0] \times 100\% \quad (2)$$

$$\Delta MR = MR90 - MR65 \quad (3)$$

L. Reversible Elongation at Absorbing Water and
Percentage of Elongation in Longitudinal Direction of Yarn:

The original length (L0) of a sample fiber is determined after drying the fiber at 60°C for 4 hours. The fiber is immersed in water at 25°C for 10 minutes and is taken out of the water, and the length of the fiber after treatment (L1) is determined immediately thereafter. The length of the fiber after drying (L2) is then determined after drying the fiber at 60°C for 4 hours. The procedure of drying and immersion in water is repeated a total of three times. The sample is evaluated to have reversible elongation at absorbing water when it shows a percentage of elongation in the longitudinal direction of the yarn in the third procedure of 50% or more of that in the first procedure. The percentage of elongation in a longitudinal direction of the yarn is determined by calculation according to the following equation. The length of the fiber is determined by binding the sample fiber with two colored yarns at an interval of about 100 mm, and measuring the length between the two yarns.

[0058]

Percentage of elongation (%) in longitudinal direction
of the yarn = $((L1 - L0)/L0) \times 100(\%)$

Example 1

A N6 (20% by weight) and a copolymerized PET (80% by weight) were melted and kneaded in a twin-screw extrusion-

kneader at 260°C to obtain polymer alloy chips. The N6 had a melt viscosity of 530 poise (262°C at a shear rate of 121.6 sec⁻¹) and a melting point of 220°C. The copolymerized PET had a melt viscosity of 3100 poise (262°C at a shear rate of 121.6 sec⁻¹) and a melting point of 225°C, had been copolymerized with 8% by mole of isophthalic acid and 4% by mole of bisphenol A. The polymer alloy chips were melted in a melting section 2 at 275°C and were introduced to a spin block 3 at a spinning temperature of 280°C. The molten polymer alloy was filtrated through a metallic nonwoven fabric having a max hole diameter of 15 µm and was subjected to melt spinning through a spinneret 5 of which surface temperature was set to 262°C (FIG. 12). The spinneret had a weighing section 12, 0.3 mm in diameter, located above an orifice, with orifice diameter 14 of 0.7 mm and orifice length 13 of 1.75 mm, as shown in FIG. 13. Discharge rate per orifice was set to 2.9 g per minute. The shear stress between the spinneret orifice and the polymer was sufficiently low at 1.5×10^5 dyne/cm² (viscosity of the polymer alloy was 1900 poise at 262°C and shear rate was 77 sec⁻¹). The distance from the bottom surface of the spinneret to the cooling start point (top end of the cooling equipment 6) was 9 cm. The discharged thread was cooled and solidified by a cooling air at 20°C over a distance of one meter, fed with an oil by an finishing guide 8 arranged 1.8 meter down the spinneret 5 and was wound through a first take-up roller 9 and a second take-up roller 10, that were not heated, at a

rate of 900 meters per minute. In this procedure, the fiber showed good spinnability and there occurred no fiber breakage during 24 hours of continuous spinning operation. The alloy fibers were subjected to heat drawing treatment with a first hot roller 17 at a temperature of 90°C and a second hot roller 18 at a temperature of 130°C (FIG. 14). Drawing ratio between the first hot roller 17 and the second hot roller 18 was set to 3.2. The polymer alloy fibers thus obtained showed good properties of 120 dtex, 12-filament, 4.0 cN/dtex in strength, 35% in elongation and $U\% = 1.7\%$. Observation of a cross section of the polymer alloy fiber under a TEM showed an islands-in-sea structure where the copolymerized PET (light portion) formed the sea and the N6 (dark portion) formed the islands (FIG. 2). The diameter of the N6 island domain by number average was 53 nm, indicating that the N6 was dispersed on the nanometer order in the polymer alloy fiber.

[0059]

The polymer alloy fibers thus obtained were formed into a round braid that was immersed in a 3% aqueous solution of sodium hydroxide (90°C, bath ratio 1:100) for 2 hours, thereby to remove 99% or more of the copolymerized PET from the polymer alloy fibers by hydrolysis. The round braid comprising solely of N6 yarn showed a macroscopic appearance of continuous filament yarn or spun yarn and maintained the form of round braid, despite the fact that the copolymerized PET constituting the sea component was removed. Moreover,

quite unlike a round braid formed from an ordinary N6 fiber, this round braid did not show the "slimy touch" of nylon but showed the "sleekness" of silk or "dry feeling" of rayon.

[0060]

A yarn was drawn out of the round braid comprising solely of N6 yarn, and was observed on the side surface of the fiber under an optical microscope. The diameter of the fiber had been reduced to about two thirds that of the state before alkali treatment, showing that the fiber shrank in the radial direction when the sea component was removed (FIG. 4). Then observation of the side surface of the fiber under an SEM showed that the yarn was not a single yarn, but an aggregate of nanofibers having morphology like spun yarn that was constituted from numerous coagulated nanofibers bonded to each other from point to point (FIG. 3). Spacing between the nanofibers in the N6 aggregate of nanofibers was from about several tens of nanometers to about 200 nm, with extremely small voids existing between the nanofibers. Picture of a cross section of the fiber under a TEM shown in FIG. 1 indicates that single fiber diameter of the N6 nanofiber is about several tens of nanometers. The nanofiber had such an unprecedented fineness as the single fiber diameter by number average was 56 nm (3×10^{-5} dtex). The fineness ratio of single fibers having single fiber fineness by number average was in a range from 1×10^{-7} to 9×10^{-5} dtex (equivalent to single fiber diameter from 1 to 100 nm) was 99%. Particularly, fineness ratio of single fibers having diameter

in a range from 55 to 84 nm was 71%, with very small spread of single fiber fineness values. Histograms of the single fiber diameters and single fiber fineness of the nanofibers determined from the TEM photograph are shown in FIG. 5 and FIG. 6. Number (frequency) and fineness ratio were determined for each section having a width of 10 nm in diameter of the single fiber. That is, single fibers having diameters in a range from 55 to 64 nm were counted as single fiber having diameter of 60 nm, and single fibers having diameters in a range from 75 to 84 nm were counted as single fiber having diameter of 80 nm.

[0061]

The measurement of the ratio of moisture adsorption (ΔMR) of the round braid consisting solely of the N6 showed a high moisture adsorbing capability of 6%, surpassing that of cotton. Further, a yarn comprising the aggregate of N6 nanofibers showed such a rate of elongation in the longitudinal direction of yarn at absorbing water, that indicated a reversible repetition of swelling upon absorbing water and shrinkage upon drying (FIG. 11). The rate of elongation in the longitudinal direction of yarn at absorbing water was 7%, far higher than 3% in the case of the ordinary N6 fiber. Measurement of mechanical properties of the yarn comprising the aggregate of N6 nanofibers showed a strength of 2.0 cN/dtex and an elongation of 50%. 140°C dry heat shrinkage ratio was 3%.

[0062]

When the round braid was buffed, it showed excellent hands providing ultra-soft feeling like peach skin, or soft and moist touch like human skin which have never been realized by the ultrafine fibers of the prior art.

[0063]

Example 2

Polymer alloy chips were obtained using a twin-screw extrusion-kneader similarly to Example 1, except for using a N6 (20% by weight) having a melt viscosity of 2120 poise (262°C at a shear rate of 121.6 sec⁻¹). The polymer chips were subjected to the melt spinning process similarly to Example 1, except for setting the discharge rate per orifice to 1.0 g per minute and shear stress between the spinneret orifice wall and the polymer at 6.7×10^4 dyne/cm² (viscosity of the polymer alloy was 2600 poise at 262°C and at a shear rate of 27 sec⁻¹). In this procedure, the fiber showed good spinnability and there occurred no fiber breakage during 24 hours of continuous spinning operation. The undrawn yarn of the polymer alloy was drawn similarly to Example 1, except for setting the drawing ratio to 3.0, thereby to obtain polymer alloy fibers having good properties of 128 dtex, 36-filament, 4.1 cN/dtex in strength, 37% in elongation and U% = 1.2%. Observation of a cross section of the polymer alloy fiber thus obtained under a TEM showed islands-in-sea structure where the copolymerized PET formed the sea and the N6 formed the islands similarly to Example 1. The diameter of the N6 island domain by number average was 40 nm,

indicating that the N6 was dispersed on the nanometer order in the polymer alloy fiber.

[0064]

The polymer alloy fibers thus obtained were subjected to alkali treatment similarly to Example 1, and an aggregate of nanofibers of morphology like spun yarn was obtained. Spread of single fiber fineness values of the nanofibers was analyzed similarly to Example 1, showing that the nanofiber had such an unprecedented fineness as the single fiber diameter by number average was 43 nm (2×10^{-5} dtex), with very small spread of single fiber fineness values.

[0065]

The ratio of moisture adsorption (ΔMR) of a round braid formed from the aggregate of nanofibers was 6%, and the rate of elongation in the longitudinal direction of yarn at absorbing water was 7%. A yarn comprising the aggregate of N6 nanofibers showed a strength of 2.2 cN/dtex and an elongation of 50%. 140°C dry heat shrinkage ratio was 3%.

[0066]

When the round braid was buffed, it showed excellent hands providing ultra-soft feeling like peach skin, or soft and moist touch like human skin which have never been realized by the ultrafine fibers of the prior art.

[0067]

Example 3

Melt spinning operation was carried out similarly to Example 2, except for using a N6 (20% by weight) having a

melt viscosity of 5000 poise (262°C at a shear rate of 121.6 sec⁻¹) and melting point of 220°C. The polymer chips were subjected to the melt spinning process similarly to Example 1, except for setting the shear stress between the spinneret orifice wall and the polymer at 1.0×10^5 dyne/cm² (viscosity of the polymer alloy was 3800 poise at 262°C and at a shear rate of 27 sec⁻¹), thereby to obtain undrawn polymer alloy yarn. In this procedure, the fiber showed good spinnability and there occurred no fiber breakage during 24 hours of continuous spinning operation. The undrawn yarn of the polymer alloy was drawn and annealed similarly to Example 2, thereby to obtain polymer alloy fibers having good properties of 128 dtex, 36-filament, 4.5 cN/dtex in strength, 37% in elongation and U% = 1.9%. Observation of a cross section of the polymer alloy fiber thus obtained under a TEM showed islands-in-sea structure where the copolymerized PET formed the sea and the N6 formed the islands similarly to Example 1. The diameter of the N6 island domain by number average was 60 nm, indicating that the N6 was dispersed on the nanometer order in the polymer alloy fiber.

[0068]

The polymer alloy fibers thus obtained were subjected to alkali treatment similarly to Example 1, and an aggregate of nanofibers of morphology like spun yarn was obtained. Spread of single fiber fineness values of the nanofibers was analyzed similarly to Example 1, showing that the nanofiber had such an unprecedented fineness as the single fiber

diameter by number average was 65 nm (4×10^{-5} dtex), with very small spread of single fiber fineness values.

[0069]

The ratio of moisture adsorption (ΔMR) of a round braid formed from the aggregate of nanofibers was 6%, and the rate of elongation in the longitudinal direction of yarn at absorbing water was 7%. A yarn comprising the aggregate of N6 nanofibers showed a strength of 2.4 cN/dtex and an elongation of 50%. 140°C dry heat shrinkage ratio was 3%.

[0070]

When the round braid was buffed, it showed excellent hands providing ultra-soft feeling like peach skin, or soft and moist touch like human skin which have never been realized by the ultrafine fibers of the prior art.

[0071]

Example 4

Melt spinning operation was carried out similarly to Example 3, except for setting the blending ratio of N6 to the polymer alloy as a whole at 50%. The melt spinning process was conducted similarly to Example 1, except for setting the shear stress between the spinneret orifice wall and the polymer at 1.2×10^5 dyne/cm², thereby to obtain undrawn polymer alloy yarn. In this procedure, the fiber showed good spinnability and there occurred no fiber breakage during 24 hours of continuous spinning operation. The undrawn yarn of the polymer alloy was drawn similarly to Example 2, thereby to obtain polymer alloy fibers having good properties of 128

dtex, 36-filament, 4.3 cN/dtex in strength, 37% in elongation and $U\% = 2.5\%$. Observation of a cross section of the polymer alloy fiber thus obtained under a TEM showed islands-in-sea structure where the copolymerized PET formed the sea and the N6 formed the islands similarly to Example 1. The diameter of the N6 island domain by number average was 80 nm, indicating that the N6 was uniformly dispersed on the nanometer order in the polymer alloy fiber.

[0072]

The polymer alloy fibers thus obtained were subjected to alkali treatment similarly to Example 1, and an aggregate of nanofibers of morphology like spun yarn was obtained. Spread of single fiber fineness values of the nanofibers was analyzed similarly to Example 1, showing that the nanofiber had such an unprecedented fineness as the single fiber diameter by number average was 84 nm (6×10^{-5} dtex), with very small spread of single fiber fineness values.

[0073]

A yarn comprising the aggregate of N6 nanofibers showed a strength of 2.6 cN/dtex and an elongation of 50%.

[0074]

Comparative Example 1

An islands-in-sea composite yarn was made according to a method described in Example 1 of Japanese Unexamined Patent Publication No. 53-106872, using a PET having a melt viscosity of 1800 poise (290°C at a shear rate of 121.6 sec⁻¹) and a melting point of 255°C as the island component, and a

polystyrene (PS) having a melt viscosity of 1000 poise (290°C at a shear rate of 121.6 sec^{-1}) and a Vicat softening temperature of 170°C as the sea component. This yarn was treated with trichloroethylene so as to remove 99% or more of the PS according to a method described in Example of Japanese Unexamined Patent Publication No. 53-106872, thereby to obtain an ultrafine yarn. TEM observation of a cross section of the fiber showed a large single fiber diameter of $2.0 \mu\text{m}$ (0.04 dtex).

[0075]

Comparative Example 2

A N6 having a melt viscosity of 500 poise (280°C at a shear rate of 121.6 sec^{-1}) and a melting point of 220°C and a PET having a melt viscosity of 2100 poise (280°C at a shear rate of 121.6 sec^{-1}) and a melting point of 255°C were blended in chips with the content of the N6 set to 20% by weight. Then melt spinning was carried out similarly to Example 1, except for melting at 290°C , setting the spinning temperature to 296°C and the surface temperature of the spinneret to 280°C and using a straight spinneret having 36 orifices, an orifice diameter of 0.30 mm and an orifice length of 50 mm. An undrawn yarn was wound at a spinning rate of 1000 m/min. Because of the simple chip blending operation and a large difference in the melting point between the polymers, a significant blending unevenness of the N6 and the PET and a significant Barus under the spinneret were observed. While the yarn could not be wound stably due to low stringiness, a

small quantity of undrawn yarn was obtained and was drawn similarly to Example 1 with temperature of the first hot roller 17 set to 85°C and the drawing ratio set to 3 times, thereby to obtain a drawn yarn of 100 dtex and 36-filament.

[0076]

This yarn was formed into a round braid similarly to Example 1, and was also subjected to alkali treatment to remove 99% or more of the PET component. A yarn comprising solely of N6 was drawn out of the round braid. TEM observation of a cross section of the fiber showed that an ultrafine yarn having single fiber diameter of 400 nm to 4 μm (single fiber fineness from 1×10^{-3} to 1×10^{-1} dtex) was formed. However, it showed single fiber fineness by number average of a large value of 9×10^{-3} dtex (single fiber diameter of 1.0 μm). The N6 ultrafine yarn also showed a large spread of single fiber fineness values.

[0077]

Comparative Example 3

A N6 having a melt viscosity of 3950 poise (262°C at a shear rate of 121.6 sec^{-1}) and a melting point of 220°C and a PE having a melt viscosity of 560 poise (262°C at a shear rate of 121.6 sec^{-1}) and a melting point of 105°C were blended in chips with the content of the N6 set to 65% by weight. Then after melting by using an apparatus shown in FIG. 15, setting the temperature of a single-screw extrusion kneader 21 at 260°C, melt spinning was carried out similarly to Example 1, except for using a straight spinneret having 12

orifices, an orifice diameter of 0.30 mm and an orifice length of 50 mm. A significant blending unevenness of the N6 and the PE and a significant Barus under the spinneret were observed. While the yarn could not be wound stably due to low stringiness, a small quantity of undrawn yarn was obtained and was drawn and was subjected to drawing and heat treatment similarly to Example 1, thereby to obtain a drawn yarn of 82 dtex and 12-filament. The drawing ratio was set to 2.0.

[0078]

This yarn was formed into a round braid similarly to Example 1, and was subjected to dissolving treatment with toluene at 85°C for one hour or more to remove 99% or more of the PE component. A yarn comprising solely of N6 was drawn out of the round braid. TEM observation of a cross section of the fiber showed that an ultrafine yarn having single fiber diameter of 500 nm to 3 μm (single fiber fineness 2×10^{-3} to 8×10^{-2} dtex) was formed. However, it showed single fiber fineness by number average of a large value of 9×10^{-3} dtex (single fiber diameter of 1.0 μm). The N6 ultrafine yarn also showed a large spread of single fiber fineness values.

[0079]

Comparative Example 4

A melt spinning operation was carried out similarly to Comparative Example 3 using an apparatus shown in FIG. 17 wherein a N6 having a melt viscosity of 1500 poise (262°C at

a shear rate of 121.6 sec^{-1}) and a melting point of 220°C and a PE having a melt viscosity of 1450 poise (262°C at a shear rate of 121.6 sec^{-1}) and a melting point of 105°C were introduced into a twin-screw extrusion-kneader while weighing the polymers separately with the content of the N6 set to 20% by weight. A significant blending unevenness of the N6 and the PE and a significant Barus under the spinneret were observed. While the yarn could not be wound stably due to low stringiness, a small quantity of undrawn yarn was obtained and was drawn and subjected to heat treatment similarly to Example 1, thereby to obtain a drawn yarn of 82 dtex and 12-filament. The drawing ratio was set to 2.0.

[0080]

This yarn was formed into a round braid similarly to Example 1, and was subjected to dissolving treatment with toluene at 85°C for one hour or more to remove 99% or more of the PE component. A yarn comprising solely of N6 was drawn out of the round braid. TEM observation of a cross section of the fiber showed that an ultrafine yarn having single fiber diameter of 100 nm to $1 \mu\text{m}$ (single fiber fineness 9×10^{-5} to 9×10^{-3} dtex) was formed. However, it showed single fiber fineness by number average of a large value of 1×10^{-3} dtex (single fiber diameter of 384 nm). The ultrafine yarn also showed a large spread of single fiber fineness values (FIG. 7, FIG. 8).

[0081]

Comparative Example 5

An islands-in-sea composite yarn was made according to a method described in Comparative Example 1 of Japanese Examined Patent Publication No. 60-28922, using a spinning pack and a spinneret shown in FIG. 11 of the aforementioned Publication and using a PS and a PET described in Comparative Example 1 of the Publication. A blended polymer of PS and PET in weight proportion of 2:1 was used as the island component and PS was used as the sea component of the islands-in-sea composite yarn. The islands-in-sea proportion was 1:1 in a weight proportion. Specifically, PET was used as component A, and PS was used as components B and C in FIG. 11 of the aforementioned Publication. This yarn was treated with trichloroethylene similarly to Comparative Example 1 of the Publication described above, so as to remove 99% or more of the PS, thereby to obtain an ultrafine yarn. An observation of a cross section of the fiber showed the existence of a trace of single fibers having diameter of about 100 nm at the minimum. However, since the PET was not dispersed satisfactorily in the PS, it showed single fiber fineness by number average of a large value of 9×10^{-4} dtex (single fiber diameter of 326 nm). The ultrafine yarn also showed a large spread of single fiber fineness values (FIG. 9, FIG. 10).

[0082]

[Table 1]

	Island polymer			Sea polymer			Shear stress at orifice (dyne/cm ²)
	Polymer	Melt viscosity (poise)	Proportion (% by weight)	Polymer	Melt viscosity (poise)	Proportion (% by weight)	
Example 1	N6	530	20	Copolymerized PET	3100	80	1.5×10^5
Example 2	N6	2120	20	Copolymerized PET	3100	80	6.7×10^4
Example 3	N6	5000	20	Copolymerized PET	3100	80	1.0×10^5
Example 4	N6	5000	50	Copolymerized PET	3100	50	1.2×10^{-5}
Comparative Example 1	PET	1800	96	PS	1000	4	-
Comparative Example 2	N6	500	20	PET	2100	80	5.1×10^5
Comparative Example 3	N6	3950	65	PE	560	35	1.5×10^6
Comparative Example 4	N6	1500	20	PE	1450	80	6.0×10^5
Comparative Example 5	PS/PET	-	50	PS	-	50	-

[0083]

[Table 2]

	Number-average		Spread		Strength (cN/dtex)
	Diameter	Fineness	Fineness ratio	Range	
	(nm)	(dtex)	(%)	Range of diameters: Fineness ratio	
Example 1	56	3×10^{-5}	99	55 - 84 nm: 71%	2.0
Example 2	43	2×10^{-5}	100	45 - 74 nm: 75%	2.2
Example 3	65	4×10^{-5}	98	65 - 94 nm: 70%	2.4
Example 4	84	6×10^{-5}	78	75 - 104 nm: 64%	2.6
Comparative Example 1	2000	4×10^{-2}	0	-	-
Comparative Example 2	1000	9×10^{-3}	0	974 - 1005 nm: 10%	-
Comparative Example 3	1000	9×10^{-3}	0	974 - 1005 nm: 10%	-
Comparative Example 4	384	1×10^{-3}	0	395 - 424 nm: 10%	-
Comparative Example 5	326	9×10^{-4}	0	395 - 424 nm: 10%	-

Fineness ratio: Fineness ratio of single fiber fineness in a range from 1×10^{-7} to 1×10^{-4} dtex

Range: Area ratio in a section 30 nm wide in diameters.

[0084]

Example 5

The N6 and the copolymerized PET used in Example 1 were separately melted at 270°C in an apparatus shown in FIG. 16, and the molten polymer was introduced into a spin block 3 having a spinning temperature of 280°C. The two polymers were carefully mixed through 104×10^4 splits in a static mixer 22 ("Hi-Mixer", available from TORAY Engineering Co., Ltd.) installed in a spinning pack 4, and melt spinning operation was carried out similarly to Example 1. The polymer consisted of 20% by weight of the N6 and 80% by weight of the copolymerized PET. The undrawn yarn was drawn and subjected to annealing similarly to Example 1. Polymer alloy fibers thus obtained showed good properties of 120 dtex, 12-filament, 3.9 cN/dtex in strength, 38% in elongation and $U\% = 1.7\%$. Observation of a cross section of the polymer alloy fiber under a TEM showed islands-in-sea structure where the copolymerized PET formed the sea and the N6 formed the islands similarly to Example 1. The diameter of the N6 island domain by number average was 52 nm, indicating that the N6 was dispersed on the nanometer order in the polymer alloy fiber.

[0085]

The polymer alloy fibers thus obtained were subjected to alkali treatment similarly to Example 1, and an aggregate of nanofibers having morphology like spun yarn was obtained. Spread of single fiber fineness values of the nanofibers was

analyzed similarly to Example 1, showing that the nanofiber had such an unprecedented fineness as the single fiber diameter by number average was 54 nm (3×10^{-5} dtex), with very small spread of single fiber fineness values.

[0086]

The ratio of moisture adsorption (ΔMR) of a round braid formed from the aggregate of nanofibers was 6%, and the rate of elongation in the longitudinal direction of yarn at absorbing water was 7%. A yarn comprising the aggregate of N6 nanofibers showed a strength of 2.0 cN/dtex and an elongation of 50%. 140°C dry heat shrinkage ratio was 3%.

[0087]

When the round braid was buffed, it showed excellent hands providing ultra-soft feeling like peach skin, or soft and moist touch like human skin which have never been realized by the ultrafine fibers of the prior art.

[0088]

Example 6

The N6 and the copolymerized PET used in Example 1 were melted, mixed and kneaded in a twin-screw extrusion-kneader at 270°C using the apparatus shown in FIG. 17, and the molten polymer was introduced into a spin block 3 having a spinning temperature of 280°C. The polymer consisted of 20% by weight of the N6 and 80% by weight of the copolymerized PET. The undrawn yarn was drawn and subjected to annealing similarly to Example 1. Polymer alloy fibers thus obtained showed good properties of 120 dtex, 12-filament, 3.9 cN/dtex in strength,

38% in elongation and $U\% = 1.7\%$. Observation of a cross section of the polymer alloy fiber under a TEM showed islands-in-sea structure where the copolymerized PET formed the sea and the N6 formed the islands similarly to Example 1. The diameter of the N6 island domain by number average was 54 nm, indicating that the N6 was dispersed on the nanometer order in the polymer alloy fiber.

[0089]

The polymer alloy fibers thus obtained were subjected to alkali treatment similarly to Example 1, and an aggregate of nanofibers having morphology like spun yarn was obtained. Spread of single fiber fineness values of the nanofibers was analyzed similarly to Example 1, showing that the nanofiber had such an unprecedented fineness as the single fiber diameter by number average was 56 nm (3×10^{-5} dtex), with very small spread of single fiber fineness values.

[0090]

The ratio of moisture adsorption (ΔMR) of a round braid formed from the aggregate of nanofibers was 6%, and the rate of elongation in the longitudinal direction of yarn at absorbing water was 7%. A yarn comprising the aggregate of N6 nanofibers showed a strength of 2.0 cN/dtex and an elongation of 50%. 140°C dry heat shrinkage ratio was 3%.

[0091]

When the round braid was buffed, it showed excellent hands providing ultra-soft feeling like peach skin, or soft and moist touch like human skin which have never been

realized by the ultrafine fibers of the prior art.

[0092]

[Table 3]

	Island polymer			Sea polymer			Order of kneading	Shear stress at orifice (dyne/cm ²)
	Polymer	Melt viscosity (poise)	Proportion (% by weight)	Polymer	Melt viscosity (poise)	Proportion (% by weight)		
Example 5	N6	530	20	Copolymerized PET	310	80	In the spinning pack	0.060
Example 6	N6	530	20	Copolymerized PET	310	80	Before the spinning pack	0.20

[0093]

[Table 4]

	Number-average		Spread		Strength (cN/dtex)
	Diameter (nm)	Fineness (dtex)	Fineness ratio (%)	Range	
				Range of diameters: Fineness ratio	
Example 5	54	3×10^{-5}	100	55 - 84 nm: 72%	2.0
Example 6	56	1.3×10^{-5}	100	55 - 84 nm: 70%	2.0

Fineness ratio: Fineness ratio of single fiber fineness in a range from 1×10^{-7} to 1×10^{-4} dtex

Range: Area ratio in a section 30 nm wide in diameters.

[0094]

Example 7

Kneading and melt spinning operations were carried out similarly to Example 1, except for using "Paogen PP-15" (melt viscosity of 3500 poise at 262°C at a shear rate of 121.6 sec⁻¹, melting point of 55°C) available from Daiichi Kogyo Seiyaku Co., Ltd., that is a polymer soluble to hot water, and setting the spinning rate to 5000 m/min, where the shear stress between the spinneret orifice wall and the polymer was 1.5×10^5 dyne/cm² (viscosity of the polymer alloy was 1900 poise at 262°C and at a shear rate of 77 sec⁻¹). The polymer alloy fibers thus obtained showed good properties of 70 dtex, 12-filament, 3.8 cN/dtex in strength, 50% in elongation and U% = 1.7%. Observation of a cross section of the polymer alloy fiber under a TEM showed islands-in-sea structure where the copolymerized PET formed the sea and the N6 formed the islands. The diameter of the N6 island domain by number average was 53 nm, indicating that the N6 was uniformly dispersed on the nanometer order in the polymer alloy fiber.

[0095]

The polymer alloy fibers thus obtained were subjected to alkali treatment similarly to Example 1, and an aggregate of nanofibers having morphology like spun yarn was obtained. Spread of single fiber fineness values of the nanofibers was analyzed similarly to Example 1, showing that the nanofiber had such an unprecedented fineness as the single fiber diameter by number average was 56 nm (3×10^{-5} dtex), with

very small spread of single fiber fineness values.

[0096]

The ratio of moisture adsorption (ΔMR) of a round braid formed from the aggregate of nanofibers was 6%, and the rate of elongation in the longitudinal direction of yarn at absorbing water was 7%. A yarn comprising the aggregate of N6 nanofibers showed a strength of 2.0 cN/dtex and an elongation of 60%.

[0097]

When the round braid was buffed, it showed excellent hands providing ultra-soft feeling like peach skin, or soft and moist touch like human skin which have never been realized by the ultrafine fibers of the prior art.

[0098]

Example 8

By using a N66 having a melt viscosity of 1000 poise (280°C at a shear rate of 121.6 sec^{-1}) and a melting point of 250°C instead of the N6 and using an apparatus shown in FIG. 11, the N66 was melted at 270°C and the polymer soluble to hot water that was used in Example 7 was melted at 80°C . The molten polymers were introduced into the spin block 3 having a spinning temperature of 280°C . The two polymers were subjected to melt spinning operation similarly to Example 5. Proportions of the polymers were 20% by weight for the N66 and 80% by weight for the polymer soluble to hot water, and discharge per orifice was set to 2.9 g per minute. Spinning rate was set to 5000 meters per minute, and the shear stress

between the spinneret orifice wall and the polymer showed sufficiently low value of 1.9×10^5 dyne/cm² (viscosity of the polymer alloy was 2500 poise at 262°C and at a shear rate of 77 sec⁻¹). The polymer alloy fibers having 70 dtex, 12-filament, 4.5 cN/dtex in strength and 45% in elongation were obtained. Observation of a cross section of the polymer alloy fiber under a TEM showed islands-in-sea structure where the polymer soluble to hot water formed the sea and the N66 formed the islands. The diameter of the N66 island domain by number average was 58 nm, indicating that the N66 was dispersed on the nanometer order in the polymer alloy fiber.

[0099]

The polymer alloy fibers thus obtained were subjected to alkali treatment similarly to Example 1, and an aggregate of nanofibers having morphology like spun yarn was obtained. Spread of single fiber fineness values of the nanofibers was analyzed similarly to Example 1, showing that the nanofiber had such an unprecedented fineness as the single fiber diameter by number average was 62 nm (3×10^{-5} dtex), with very small spread of single fiber fineness values.

[0100]

The ratio of moisture adsorption (ΔMR) of a round braid formed from the aggregate of nanofibers was 6%, and the rate of elongation in the longitudinal direction of yarn at absorbing water was 7%. A yarn comprising the aggregate of N6 nanofibers showed a strength of 2.5 cN/dtex and an elongation of 60%.

[0101]

When the round braid was buffed, it showed excellent hands providing ultra-soft feeling like peach skin, or soft and moist touch like human skin which have never been realized by the ultrafine fibers of the prior art.

[0102]

Example 9

A copolymerized PET and a polymer soluble to hot water were mixed, kneaded and melt-spun similarly to Example 6, except for using the copolymerized PET (8% by weight of PEG 1000 and 7% by mole of isophthalic acid were copolymerized) having a melt viscosity of 3000 poise (262°C at a shear rate of 121.6 sec⁻¹) and a melting point of 225°C, and using the polymer soluble to hot water that was used in Example 7. Proportions of the polymers were 20% by weight for the copolymerized PET and 80% by weight for the polymer soluble to hot water, and discharge per orifice was set to 1.0 g per minute. Spinning rate was set to 6000 meters per minute. Shear stress between the spinneret orifice and the polymer showed a sufficiently low value of 8.6×10^4 dyne/cm² (viscosity of the polymer alloy was 3200 poise at 262°C and at a shear rate of 27 sec⁻¹). The polymer alloy fibers having 60 dtex, 36-filament, 3.0 cN/dtex in strength and 55% in elongation were obtained. Observation of a cross section of the polymer alloy fiber under a TEM showed islands-in-sea structure where the polymer soluble to hot water formed the sea and the copolymerized PET formed the islands. The

diameter of the copolymerized PET island domain by number average was 52 nm, indicating that the copolymerized PET was dispersed on the nanometer order in the polymer alloy fiber.

[0103]

The polymer alloy fibers thus obtained were formed into a round braid similarly to Example 1, and was treated with hot water at 100°C so as to dissolve the polymer soluble to hot water. The round braid thus formed from the aggregate of nanofibers had sleekness of silk or dry feeling of rayon. Spread of single fiber fineness values of the nanofibers was analyzed similarly to Example 1, showing that the nanofiber had such an unprecedented fineness as the single fiber diameter by number average was 54 nm (3×10^{-5} dtex), with very small spread of single fiber fineness values.

[0104]

The ratio of moisture adsorption (ΔMR) of the round braid formed from the aggregate of nanofibers was 2%. A yarn comprising the aggregate of nanofibers of the N6 showed a strength of 1.5 cN/dtex and an elongation of 70%.

[0105]

Example 10

Kneading and melt spinning operations were carried out similarly to Example 9, except for using a PET having a melt viscosity of 1900 poise (280°C, at a shear rate of 121.6 sec^{-1}) and a melting point of 255°C, and using the polymer soluble to hot water that was used in Example 7. Proportions of the polymers were 20% by weight for the PET and 80% by

weight for the polymer soluble to hot water. Melting temperature of the PET was set at 285°C, melting temperature of the polymer soluble to hot water was set at 80°C, and discharge per orifice was set to 1.0 g per minute. Shear stress between the spinneret orifice and the polymer showed a sufficiently low value of 8.8×10^4 dyne/cm² (viscosity of the polymer alloy was 3300 poise at 262°C and at a shear rate of 27 sec⁻¹). The polymer alloy fibers having 60 dtex, 36-filament, 3.0 cN/dtex in strength and 45% in elongation were obtained. Observation of a cross section of the polymer alloy fiber under a TEM showed islands-in-sea structure where the polymer soluble to hot water formed the sea and the PET formed the islands. The diameter of the PET island domain by number average was 62 nm, indicating that the PET was dispersed on the nanometer order in the polymer alloy fiber.

[0106]

An aggregate of nanofibers was formed in a process similar to that of Example 9 using the polymer alloy fibers thus obtained. The nanofiber had such an unprecedented fineness as the single fiber diameter by number average was 65 nm (3×10^{-5} dtex), with very small spread of single fiber fineness values.

[0107]

Example 11

Kneading and melt spinning operations were carried out similarly to Example 9, except for using a PBT having a melt viscosity of 1200 poise (262°C at a shear rate of 121.6 sec⁻¹)

and a melting point of 225°C, and using the polymer soluble to hot water that was used in Example 7. Proportions of the polymers were 20% by weight for the PBT and 80% by weight for the polymer soluble to hot water. Melting temperature of the PBT was set at 255°C, melting temperature of the polymer soluble to hot water was set at 80°C, spinning temperature was 265°C, and discharge per orifice was set to 1.0 g per minute. Shear stress between the spinneret orifice and the polymer showed a sufficiently low value of 7.5×10^5 dyne/cm² (viscosity of the polymer alloy was 2800 poise at 250°C and at a shear rate of 27 sec⁻¹). The polymer alloy fibers having 60 dtex, 36-filament, 3.0 cN/dtex in strength and 45% in elongation were obtained. Observation of a cross section of the polymer alloy fiber under a TEM showed islands-in-sea structure where the polymer soluble to hot water formed the sea and the PBT formed the islands. The diameter of the PBT island domain by number average was 62 nm, indicating that the PBT was dispersed on the nanometer order in the polymer alloy fiber.

[0108]

An aggregate of nanofibers was formed in a process similar to that of Example 9 using the polymer alloy fibers thus obtained. The nanofiber had such an unprecedented fineness as the single fiber diameter by number average was 65 nm (4×10^{-5} dtex), with very small spread of single fiber fineness values.

[0109]

Example 12

Kneading and melt spinning operations were carried out similarly to Example 9, except for using a PTT having a melt viscosity of 2200 poise (262°C at a shear rate of 121.6 sec⁻¹) and a melting point of 225°C, and using the polymer soluble to hot water that was used in Example 7. Shear stress between the spinneret orifice and the polymer showed a sufficiently low value of 9.4×10^4 dyne/cm² (viscosity of the polymer alloy was 3500 poise at 250°C and at a shear rate of 27 sec⁻¹). The polymer alloy fibers having 60 dtex, 36-filament, 3.0 cN/dtex in strength and 45% in elongation were obtained. Observation of a cross section of the polymer alloy fiber under a TEM showed islands-in-sea structure where the polymer soluble to hot water formed the sea and the PTT formed the islands. The diameter of the PBT island domain by number average was 62 nm, indicating that the PTT was dispersed on the nanometer order in the polymer alloy fiber.

[0110]

An aggregate of nanofibers was formed in a process similar to that of Example 9 using the polymer alloy fibers thus obtained. The nanofiber had such an unprecedented fineness as the single fiber diameter by number average was 65 nm (4×10^{-5} dtex), with very small spread of single fiber fineness values.

[0111]

Example 13

Kneading and melt spinning operations were carried out

similarly to Example 9, except for using a PLA having a melt viscosity of 3500 poise (220°C at a rate of shear of 121.6 sec⁻¹) and a melting point of 170°C, and using the polymer soluble to hot water that was used in Example 7. Proportions of the polymers were 20% by weight for the PLA and 80% by weight for the polymer soluble to hot water. Spinning temperature was 235°C, surface temperature of the spinneret was 220°C, and discharge per orifice was set to 1.0 g per minute. Shear stress between the spinneret orifice and the polymer showed a sufficiently low value of 1.2×10^5 dyne/cm² (viscosity of the polymer alloy was 4600 poise at 220°C and at a shear rate of 27 sec⁻¹). The polymer alloy fibers having 60 dtex, 36-filament, 2.5 cN/dtex in strength and 35% in elongation were obtained. Observation of a cross section of the polymer alloy fiber thus obtained under a TEM showed islands-in-sea structure where the polymer soluble to hot water formed the sea and the PLA formed the islands. The diameter of the PLA island domain by number average was 48 nm, indicating that the PLA was dispersed on the nanometer order in the polymer alloy fiber.

[0112]

An aggregate of nanofibers was formed in a process similar to that of Example 9 using the polymer alloy fibers thus obtained. The nanofiber had such an unprecedented fineness as the single fiber diameter by number average was 50 nm (2×10^{-5} dtex), with very small spread of single fiber fineness values.

[0113]

[Table 5]

	Island polymer			Sea polymer			Order of kneading
	Polymer	Melt viscosity (poise)	Proportion (% by weight)	Polymer	Melt viscosity (poise)	Proportion (% by weight)	
Example 7	N6	530	20	Polymer soluble to hot water	3500	80	Kneaded to chips
Example 8	N66	1000	20	Polymer soluble to hot water	2200	80	In the spinning pack
Example 9	Copolymerized PET	3000	20	Polymer soluble to hot water	3500	80	Before the spinning pack
Example 10	PET	1900	20	Polymer soluble to hot water	2200	80	In the spinning pack
Example 11	PBT	1200	20	Polymer soluble to hot water	3500	80	In the spinning pack
Example 12	PTT	2200	20	Polymer soluble to hot water	3500	80	In the spinning pack
Example 13	PLA	3500	20	Polymer soluble to hot water	6000	80	In the spinning pack

[Table 6]

	Number-average		Spread		Strength (cN/dtex)
	Diameter (nm)	Fineness (dtex)	Fineness ratio (%)	Range Range of diameters: Fineness ratio	
Example 7	56	3×10^{-5}	99*	55 - 84 nm: 72%	2.0
Example 8	62	3×10^{-5}	98	55 - 84 nm: 68%	2.5
Example 9	54	3×10^{-5}	99	55 - 84 nm: 71%	2.0
Example 10	65	5×10^{-5}	98	55 - 84 nm: 65%	2.0
Example 11	65	4×10^{-5}	98	55 - 84 nm: 65%	2.0
Example 12	65	4×10^{-5}	98	55 - 84 nm: 65%	2.0
Example 13	50	2×10^{-4}	100	45 - 74 nm: 72%	1.9

Fineness ratio: Fineness ratio of single fiber fineness in a range from 1×10^{-7} to 1×10^{-4} dtex

Range: Fineness ratio in a section 30 nm wide in diameters.

[0115]

Example 14

Kneading and melt spinning operations were carried out similarly to Example 8, except for using a polycarbonate (PC) having a melt viscosity of 3000 poise (262°C at a shear rate of 121.6 sec⁻¹) and a Vicat softening temperature of 150°C, and using the polymer soluble to hot water that was used in Example 7. Proportions of the polymers were 20% by weight for the PC and 80% by weight for the polymer soluble to hot water. Discharge per orifice was set to 1.0 g per minute. Shear stress between the spinneret orifice and the polymer showed a sufficiently low value of 8.8×10^4 dyne/cm² (viscosity of the polymer alloy was 3300 poise at 262°C and at a shear rate of 27 sec⁻¹). The polymer alloy fibers having 70 dtex, 36-filament, 2.2 cN/dtex in strength and 35% in elongation were obtained. Observation of a cross section of the polymer alloy fiber thus obtained under a TEM showed islands-in-sea structure where the polymer soluble to hot water formed the sea and the PC formed the islands. The diameter of the PC island domain by number average was 85 nm, indicating that the PC was dispersed on the nanometer order in the polymer alloy fiber.

[0116]

A round braid was formed in a process similar to that of Example 1 using the polymer alloy fibers thus obtained. The round braid was treated in warm water of 40°C for 10 hours so as to dissolve 99% or more of the polymer soluble to

hot water, thereby to obtain an aggregate of nanofibers. The nanofiber had such an unprecedented fineness as the single fiber diameter by number average was 88 nm (8×10^{-5} dtex), with very small spread of single fiber fineness values.

[0117]

Example 15

Kneading and melt spinning operations were carried out similarly to Example 8, except for using polymethylpentene (PMP) having a melt viscosity of 3000 poise (262°C at a shear rate of 121.6 sec^{-1}) and a melting point of 220°C and a PS having a melt viscosity of 3000 poise (262°C at a shear rate of 121.6 sec^{-1}) and a Vicat softening temperature of 105°C, and setting the spinning speed to 1500 meters per minute. Then drawing and annealing operations were carried out similarly to Example 1 by setting the drawing ratio to 1.5. Proportions of the polymers were 20% by weight for the PMP and 80% by weight for the PS, and discharge per orifice was set to 1.0 g per minute. Shear stress between the spinneret orifice and the polymer showed a sufficiently low value of $7.5 \times 10^4 \text{ dyne/cm}^2$ (viscosity of the polymer alloy was 2800 poise at 262°C and at a shear rate of 27 sec^{-1}). The polymer alloy fibers having 77 dtex, 36-filament, 3.0 cN/dtex in strength and 40% in elongation were obtained. Observation of a cross section of the polymer alloy fiber under a TEM showed islands-in-sea structure where the PS formed the sea and the PMP formed the islands. The diameter of the PMP island domain by number average was 70 nm, indicating that the PMP

was dispersed on the nanometer order in the polymer alloy fiber.

[0118]

The polymer alloy fibers thus obtained were formed into a round braid similarly to Example 1, and was treated with concentrated hydrochloric acid at 40°C so as to embrittle the PS. Then the PS was removed by methyl ethyl ketone, thereby to obtain a round braid constituted from the aggregate of PMP nanofibers. The nanofiber had such an unprecedented fineness as the single fiber diameter by number average was 73 nm (5×10^{-5} dtex), with very small spread of single fiber fineness values.

[0119]

Example 16

Kneading, melt spinning, drawing and annealing operations were carried out similarly to Example 15, except for using a PP having a melt viscosity of 3000 poise (220°C at a shear rate of 121.6 sec^{-1}) and a melting point of 162°C and the polymer soluble to hot water used in Example 7. Proportions of the polymers were set to 20% by weight for the PP and 80% by weight for the polymer soluble to hot water. Spinning temperature was set to 235°C, surface temperature of the spinneret was set to 220°C, and discharge per orifice was set to 1.0 g per minute. Shear stress between the spinneret orifice and the polymer showed a sufficiently low value of $1.2 \times 10^5 \text{ dyne/cm}^2$ (viscosity of the polymer alloy was 4600 poise at 220°C and at a shear rate of 27 sec^{-1}). The polymer

alloy fibers having 77 dtex, 36-filament, 2.5 cN/dtex in strength and 50% in elongation were obtained. Observation of a cross section of the polymer alloy fiber under a TEM showed islands-in-sea structure where the polymer soluble to hot water formed the sea and the PP formed the islands. The diameter of the PP island domain by number average was 48 nm, indicating that the PP was dispersed on the nanometer order in the polymer alloy fiber..

[0120]

The polymer alloy fibers thus obtained were formed into an aggregate of nanofibers in a process similar to Example 9. The nanofiber had such an unprecedented fineness as the single fiber diameter by number average was 50 nm (2×10^{-5} dtex), with very small spread of single fiber fineness values.

[0121]

Example 17

Kneading, melt spinning, drawing and annealing operations were carried out similarly to Example 15, except for using a polyphenylene sulfide (PPS) having a melt viscosity of 2000 poise (300°C at a shear rate of 121.6 sec⁻¹) and a melting point of 280°C and a N6 having a melt viscosity of 2000 poise (300°C at a shear rate of 121.6 sec⁻¹). Proportions of the polymers were set to 20% by weight for the PPS and 80% by weight for the N6. Melting point of the PPS was set to 320°C, melting point of the N6 was set to 270°C, spinning temperature was set to 320°C, surface temperature of the spinneret was set to 300°C, and discharge per orifice was

set to 1.0 g per minute. Shear stress between the spinneret orifice and the polymer showed a sufficiently low value of 4.8×10^4 dyne/cm² (viscosity of the polymer alloy was 1800 poise at 300°C and at a shear rate of 27 sec⁻¹). The polymer alloy fibers having 77 dtex, 36-filament, 5.2 cN/dtex in strength and 50% in elongation were obtained. Observation of a cross section of the polymer alloy fiber thus obtained under a TEM showed islands-in-sea structure where the N6 formed the sea and the PPS formed the islands. The diameter of the PPS island domain by number average was 65 nm, indicating that the PPS was dispersed on the nanometer order in the polymer alloy fiber.

[0122]

A round braid was formed in a process similar to that of Example 1 using the polymer alloy fibers thus obtained. The round braid was treated with formic acid so as to dissolve the N6, thereby to obtain a round braid constituted from an aggregate of PPS nanofibers. The nanofiber had such an unprecedented fineness as the single fiber diameter by number average was 68 nm (5×10^{-5} dtex), with very small spread of single fiber fineness values.

[0123]

[Table 7]

	Island polymer			Sea polymer			Order of kneading
	Polymer	Melt viscosity (poise)	Proportion (% by weight)	Polymer	Melt viscosity (poise)	Proportion (% by weight)	
Example 14	PC	3000	20	Polymer soluble to hot water	3500	80	In the spinning pack
Example 15	PMP	3000	20	PS	3000	80	In the spinning pack
Example 16	PP	3000	20	Polymer soluble to hot water	6000	80	In the spinning pack
Example 17	PPS	2000	20	N6	2000	80	In the spinning pack

[0124]

[Table 8]

	Number-average		Spread		Strength (cN/dtex)
	Diameter	Fineness	Fineness ratio	Range	
	(nm)	(dtex)	(%)	Range of diameters: Fineness ratio	
Example 14	88	8×10^{-5}	65	85 - 114 nm: 70%	1.5
Example 15	73	5×10^{-5}	94	65 - 94 nm: 72%	1.7
Example 16	50	2×10^{-5}	100	45 - 74 nm: 72%	1.5
Example 17	68	5×10^{-5}	92	65 - 94 nm: 68%	3.0

Fineness ratio: Fineness ratio of single fiber fineness in a range from 1×10^{-7} to 1×10^{-4} dtex

Range: Fineness ratio in a section 30 nm wide in diameters.

[0125]

Example 18

The polymer alloy fibers made in Examples 1 to 13 were woven into plain weaves. The weaves were scoured in hot water at 100°C (bath ratio 1:100) including a surfactant (GRANUP® manufactured by Sanyo Chemical Industries, Ltd.) and sodium carbonate each in concentration of 2 g per liter. Duration of scouring was set to 40 minutes for the weaves made from the yarns of Examples 1 to 6 (comprising sea component formed from copolymerized PET), and 90 minutes for the weaves made from the yarns of Examples 7 to 13 (comprising sea component formed from polymer soluble to hot water). In this process, 99% or more of the polymer soluble to hot water was removed. This was followed by an intermediate heat-setting at 140°C (intermediate heat-setting at 170°C only for the weave formed from the yarn of Example 10). The weaves made from the yarns of Examples 1 to 6 were subjected to alkali treatment by means of 3% aqueous solution of sodium hydroxide (90°C, bath ratio 1:100) for 90 minutes, thereby to remove 99% or more of the copolymerized PET, or the sea component. This was followed by final heat-setting at 140°C (final heat-setting at 170°C only for the weave formed from the yarn of Example 10). Cloths thus obtained were dyed by an ordinary method, and every one of the cloths made a beautifully dyed cloth without any dyeing unevenness. The woven fabric made from the aggregate of nanofibers had excellent hands such as "sleekness" of silk or "dry feeling"

of rayon. They also showed a high ratio of moisture adsorption (ΔMR) of 6% in the case of the woven fabric formed from the yarns of Examples 1 to 8, and 2% in the case of the woven fabric formed from the yarns of Example 9, indicating the capability to produce comfortable clothes. Furthermore, when buffed, the woven fabric showed ultra-soft feeling like peach skin, or soft and moist touch like human skin which had never been realized with the conventional ultrafine fibers.

[0126]

Comparative Example 6

The N6-blended fibers made in Comparative Examples 2 to 4 were woven into plain weaves similarly to Example 18. Only poor woven fabrics with much fluff and low surface quality could be made because the yarn had thick-thin unevenness in the longitudinal direction of yarn and much fluff due to unstable spinning. These woven fabrics were scoured followed by intermediate heat-setting. The woven fabric formed from the yarn of Comparative Example 2 was subjected to alkali treatment followed by the final heat-setting similarly to Example 18, and was dyed by the ordinary method. The woven fabric formed from the yarns of Comparative Examples 3 and 4 were immersed in toluene at 85°C for 60 minutes to remove 99% or more of the PE by dissolution. These woven fabrics were subjected to the final heat-setting and were dyed by the ordinary method. The cloths thus obtained had poor quality with much dyeing unevenness and fluff. Hands of these woven fabrics were similar to those of the convention ultrafine

yarn without sleekness and dry feeling, and had a ratio of moisture adsorption ($\Delta MR = 2\%$) similar to that of the conventional N6 fiber.

[0127]

Example 19

The polymer alloy fibers made in Examples 1 through 13 were formed into high-density plain weaves, and plain weaves constituted from the aggregate of nanofibers were obtained similarly to Example 18. A wiping cloth was made by buffing this woven fabric. The wiping cloth had higher wiping performance than a wiping cloth made from the conventional ultrafine fibers, showing satisfactory performance as a wiping cloth.

[0128]

Example 20

The polymer alloy fibers made in Examples 1 through 6 were mechanically crimped, and the crimped yarn was cut into fiber segments having a length of 51 mm, separated by means of carding, and was formed into a web with a cross-wrap webber. The web was subjected to needle punching to form a nonwoven fabric of entangled fibers having mass per unit area of 750 g/m^2 . This nonwoven fabric was impregnated with a solution consisting of 13% by weight of a polyurethane compound (abbreviated as PU) including polyether-based polyurethane as the main component and 87% by weight of N,N'-dimethylformamide (abbreviated as DMF), and the PU was solidified in an aqueous solution having DMF content of 40%

by weight. After washing in water, the nonwoven fabric was subjected to alkali treatment in a 3% aqueous solution of sodium hydroxide (60°C, bath ratio 1:100) for 2 hours, thereby to remove 99% or more of the copolymerized PET from the polymer alloy fibers, and obtain a nanofiber structure constituted from the aggregate of N6 nanofibers and the PU having thickness of about 1 mm. The nanofiber structure was buffed on one side thereof with sand paper to reduce the thickness to 0.8 mm, The other side of this fabric was processed with an emery buffer machine, thereby to form an artificially raised surface of the aggregate of nanofibers that was then dyed and finished to produce a suede-like synthetic leather. The article thus obtained had excellent appearance with no dyeing unevenness nor a problem in the mechanical properties. It also provided softer and finer touch compared to a synthetic leather made by using the conventional ultrafine fibers. It also had good moisture adsorbing capability, resulting in soft and moist touch like human skin which could not be provided by the conventional synthetic leather.

[0129]

Comparative Example 7

The N6/PE blended fiber made in Comparative Example 3 was mechanically crimped and was cut into fiber segments having a length of 51 mm, separated by means of carding, and was formed into a web with a cross-wrap webber. The web was subjected to needle punching, thereby to form a nonwoven

fabric of entangled fibers having mass per unit area of 500 g/m². The nonwoven fabric of entangled fibers was impregnated with a solution consisting of 13% by weight of a polyurethane compound (PU) including polyether-based polyurethane as the main component and 87% by weight of N,N'-dimethylformamide (DMF), and the PU was solidified in an aqueous solution having DMF content of 40% by weight. After washing in water, the fibrous material was processed with tetrachloroethylene, thereby to obtain a fibrous material formed from the N6 ultrafine yarn and the PU having thickness of about 1 mm. One side of this fibrous material was buffed with a sand paper to reduce the thickness to 0.8 mm. The other side of the fibrous material was processed with an emery buffer machine, thereby to form an artificially raised surface of the aggregate of nanofibers that was then dyed and finished to produce a suede-like synthetic leather. The article thus obtained was nothing more than an imitation of suede, with hands no better than that of the synthetic leather made from the conventional ultrafine fibers.

[0130]

Example 21

The polymer alloy fibers made in Examples 1 through 6 were mechanically crimped, and the crimped yarn was cut into fiber segments having a length of 51 mm, separated by means of carding, and was formed into a web with a cross-wrap webber. The web was subjected to needle punching to form a nonwoven fabric of entangled fibers having mass per unit area

of 750 g/m². This nonwoven fabric was impregnated with a solution consisting of 13% by weight of a polyurethane compound (abbreviated as PU) including polyether-based polyurethane as the main component and 87% by weight of N,N'-dimethylformamide (abbreviated as DMF), and the PU was solidified in an aqueous solution having DMF content of 40% by weight. After washing in water, the nonwoven fabric was subjected to alkali treatment in a 3% aqueous solution of sodium hydroxide (60°C, bath ratio 1:100) for 2 hours, thereby to remove 99% or more of the copolymerized PET from the polymer alloy fibers, and obtain a matrix of polishing material comprising a nanofiber structure constituted from the aggregate of N6 nanofibers and the PU, with PU content of 40% by weight. The fibrous material was cut into two parts, and buffed on the surface with sand papers having grades of JIS #240, #350 and #500. The fibrous material was then nipped by heating rollers, coated with fluorocarbon resin, that were disposed one upon another with a gap of 1.0 mm therebetween and kept at a temperature of 150°C, so as to press the fabric with a pressure of 0.7 kg/cm². Then the fabric was cooled quickly with a quenching roller of surface temperature 15°C, thereby to obtain a texturing cloth with smoothed surface. Results of evaluating this texturing cloth under the conditions described below are shown in Table 9. This texturing cloth made the textured surface smoother with less scratches than in the case of one made from the conventional ultrafine yarns, thus demonstrating excellent

texturing performance.

[0131]

<Evaluation of texturing: texturing of hard disk>

Work: A substrate made of a commercially available aluminum plate, coated with Ni-P plating and polished.

(Mean surface roughness was 0.28 nm)

Texturing conditions: The substrate was set on a texture apparatus and was textured under the following conditions.

[0132]

Abrasive particles: Slurry of free abrasive particles made of diamond having mean particle size of 0.1 μm .

Dripping rate: 4.5 ml per minute

Rotation speed: 1000 rpm

Tape speed: 6 cm/min.

Texturing cycle: 300 horizontal vibrations per minute with amplitude of 1 mm.

Number of samples: 30 substrates per trial

<Mean surface roughness R_a of work>

Surface roughness R_a of 30 substrates per trial was measured using an atomic force microscope (AFM) available from Veeco Inc. that was surrounded by a sound insulator and installed in a clean room controlled to a temperature of 20°C and a relative humidity of 50%, to determine the mean surface roughness R_a . Measurement was made over an area of 5 μm by 5 μm around each of two points selected at symmetrical positions with respect to the center of the disk, located at

a distance of half the radius from the center.

[0133]

<Number of scratches>

Number of scratches (X) on the surface of each sample was counted by observing under an interference microscope available from ZYGO Inc. Scratches were counted when the size was not smaller than 0.1 μm by 100 μm . Based on the measurements of 30 substrates per trial, scratch count β is defined as follows using a point y determined from the number of scratches.

[0134]

When $X \leq 4$: $y = X$

When $X \geq 5$: $y = 5$

$\beta = \sum y_i$ ($i = 1$ to 30)

$\sum y_i$ represents the total number of scratches for 30 samples.

[0135]

Comparative Example 8

The N6/PE blended fiber made in Comparative Example 3 was mechanically crimped and was cut into fiber segments having a length of 51 mm, separated by means of carding, and was formed into a web with a cross-wrap webber. The web was subjected to needle punching, thereby to form a nonwoven fabric of entangled fibers having mass per unit area of 500 g/m^2 . The nonwoven fabric of entangled fibers was impregnated with a solution consisting of 13% by weight of a polyurethane compound (PU) including polyether-based polyurethane as the

main component and 87% by weight of N,N'-dimethylformamide (DMF), and the PU was solidified in an aqueous solution having DMF content of 40% by weight. After washing in water, the fibrous material was processed with tetrachloroethylene, thereby to obtain a matrix of polishing material comprising a nanofiber structure constituted from the aggregate of N6 nanofibers and the PU. The matrix of polishing material was processed similarly to Example 22, thereby to obtain a texturing cloth. Evaluation of this texturing cloth showed $R_a = 1.6$ nm and $\beta = 32$, indicating that this texturing cloth had poor texturing performance with lower smoothness of the textured surface and more scratches than in the case of the texturing cloth made from the aggregate of nanofibers.

[0136]

[Table 9]

	Raw yarn	R_a (nm)	β (counts/30 substrates)
Example 21	Example 1	0.09	2
	Example 2	0.09	2
	Example 3	0.10	2
	Example 4	0.18	3
	Example 5	0.09	2
	Example 6	0.09	2
Comparative Example 8	Comparative Example 7	1.60	32

[0137]

Example 22

The polymer alloy fiber made in Example 1 was

mechanically crimped, and the crimped yarn was cut into fiber segments having a length of 51 mm, separated by means of carding, and was formed into a web with a cross-wrap webber. The web was subjected to needle punching to form a nonwoven fabric of entangled fibers having mass per unit area of 350 g/m². This nonwoven fabric was subjected to alkali treatment in a 3% aqueous solution of sodium hydroxide (60°C, bath ratio 1:100) for 2 hours, thereby to remove 99% or more of the copolymerized PET from the polymer alloy fibers, and obtain a nonwoven fabric of N6 nanofibers. Five disks 4.7 cm in diameter were cut out of the nonwoven fabric of N6 nanofibers and were placed one on another in a circular filter column, through which a bovine blood including white blood cells (5700 cells per microliter) was caused to flow at a rate of 2 milliliters per minute. Duration before the pressure loss reached 100 mmHg was 100 minutes, and spherical cell removal ratio at this time was 99% or higher and lymph cell removal ratio was 60%, thus proving a capability to select the spherical white blood cells related to inflammation. This is supposedly the effect of the voids existing between the nanofibers.

[0138]

Example 23

A bovine blood serum including 15 milliliters of endotoxin was caused to flow through 0.5 g of the nonwoven fabric of nanofibers that had been made in Example 22 and sterilized in an autoclave, so as to evaluate the capability

of adsorption (at 37°C, 2 hours). The concentration of endotoxin LPS decreased from 10.0 ng per milliliter to 1.5 ng per milliliter, indicating a high adsorption capability. This is supposedly because the active surface area of the nanofibers, that is far greater than that of the conventional nylon fibers, provides far more amino-terminals than in the conventional nylon fibers.

[0139]

Example 23

A spun-bonded nonwoven fabric was made using the same combination of polymers as in Example 13 and an apparatus shown in FIG. 18. Melting temperature was set to 225°C, spinning temperature was set to 230°C, and spinneret surface temperature was set to 217°C in the twin-screw extrusion-kneader 23. The spinneret of the same specifications as in Example 1 was used with discharge per orifice of 0.8 g per minute and the distance from the bottom surface of the spinneret to the cooling start point being set to 12 cm.

[0140]

The nonwoven fabric of polymer alloy thus obtained was treated in warm water of 60°C for 2 hours so as to remove 99% or more of the polymer soluble to hot water by dissolution, thereby to obtain a nonwoven fabric made from the PLA nanofibers. The diameter of the nanofiber single fiber by number average was 50 nm (2×10^{-5} dtex). Fineness ratio of single fibers having fineness in a range from 1×10^{-7} to 1×10^{-4} dtex was 98% or more, and fineness ratio of single fiber

having diameters that fall in a range from 45 to 74 nm was 70%.

[0141]

[Effect of the Invention]

The aggregate of nanofibers of the present invention having little spread of single fiber fineness values makes it possible to produce cloths of unprecedented hands and a texturing cloth of high performance.

[Brief Description of the Drawings]

FIG. 1 is a TEM micrograph showing a cross section of fibers of an aggregate of nylon nanofibers according to Example 1 of the present invention.

FIG. 2 is a TEM micrograph showing a cross section of polymer alloy fibers according to Example 1 of the present invention.

FIG. 3 is an SEM micrograph showing the state of side view of fibers of an aggregate of nanofibers according to Example 1 of the present invention.

FIG. 4 is an optical micrograph showing the state of side view of fibers of the aggregate of nanofibers according to Example 1 of the present invention.

FIG. 5 is a graph showing the spread of single fiber fineness values of the nanofibers according to Example 1 of the present invention.

FIG. 6 is a graph showing the spread of single fiber fineness values of the nanofibers according to Example 1 of

the present invention.

FIG. 7 is a graph showing the spread of single fiber fineness values of ultrafine fibers according to Comparative Example 4.

FIG. 8 is a graph showing the spread of single fiber fineness values of the ultrafine fibers according to Comparative Example 4.

FIG. 9 is a graph showing the spread of single fiber fineness values of ultrafine fibers according to Comparative Example 5.

FIG. 10 is a graph showing the spread of single fiber fineness values of the ultrafine fibers according to Comparative Example 5

FIG. 11 is a graph showing reversible elongation/contraction at absorbing water in Example 1 of the present invention.

FIG. 12 is a diagram showing a spinning machine.

FIG. 13 is a diagram showing a spinneret.

FIG. 14 is a diagram showing a drawing machine.

FIG. 15 is a diagram showing a spinning machine.

FIG. 16 is a diagram showing a spinning machine.

FIG. 17 is a diagram showing a spinning machine.

FIG. 18 is a diagram showing a spun bond spinning machine.

[Description of Reference Numerals]

1: hopper

2: melting section

- 3: spin block
- 4: spinning pack
- 5: spinneret
- 6: cooling equipment
- 7: line of thread
- 8: thread-collecting finishing guide
- 9: first take-up roller
- 10: second take-up roller
- 11: wound yarn
- 12: weighing section
- 13: orifice length
- 14: orifice diameter
- 15: undrawn yarn
- 16: feed roller
- 17: first hot roller
- 18: second hot roller
- 19: third roller (room temperature)
- 20: drawn yarn
- 21: single-screw extrusion-kneader
- 22: static mixer
- 23: twin-screw extrusion-kneader
- 24: chip weighing machine
- 25: ejector
- 26: fiber separating plate
- 27: separated line of thread
- 28: collector

[Name of Document] Abstract

[Abstract]

[Object] To provide an aggregate of nanofibers having little spread of single fiber fineness values unprecedented in the prior art.

[Solution Means] The present invention is an aggregate of nanofibers wherein single fiber fineness by number average is in a range from 1×10^{-7} to 1×10^{-4} dtex and single fibers of 60%, in fineness ratio, or more of single fibers are in a range from 1×10^{-7} to 1×10^{-4} dtex in single fiber fineness, having a morphology like filament-yarn and/or a morphology like spun yarn, and an aggregate of nanofibers made through polycondensation wherein the single fiber fineness by number average is in a range from 1×10^{-7} to 1×10^{-4} dtex and single fibers of 60%, in fineness ratio, or more of single fibers are in a range from 1×10^{-7} to 1×10^{-4} dtex in single fiber fineness.

[Selected Drawing] FIG. 1